Introduction

Processing of high-solids slurries will be necessary for the economic operation of lignocellulosic biorefineries. In this work, we examine the changing yield stress and viscosity of high-solids dilute acid pretreated corn stover (PCS) during enzymatic saccharification. PCS slurries containing 20% (w/w) insoluble solids were observed to liquefy to the point of being pourable after about two days, at a biomass conversion of about 40%. Mass balance and semi-empirical relationships were developed to connect the progress of enzymatic hydrolysis with particle concentration and yield stress, and the rheological properties of unsaccharified and saccharified PCS agree well when compared at equivalent volume fractions of insoluble particles.

Rheometry

Vane-in-cup geometry:

- 28 mm
- 42 mm
- 60 mm

Parallel plate geometry:

- 10 mm
- 20 mm
- 30 mm

Rotational speed or torque of upper plate controlled

Because the yield stress drops with conversion, indicating when a suspension becomes “pumpable”, this work will help the process designer identify an optimal residence time during saccharification. In this work, we also present preliminary results suggesting that viscosity-modification / flow-assurance additives may significantly reduce the yield stress and viscosity of PCS slurries, ensuring their downstream processability.

Enzymatic Saccharification

- High-solids bioreactor (HSBR)
  - Horizontal reactor with impellers to mix PCS and enzymes at 48°C
- Roller bottle reactor (RBR)
  - 2 L roller bottles containing 1000 g PCS
  - Incubated at 48°C
  - Rotated at 2 – 20 rotations / minute
  - 20% (w/w) washed PCS
  - 5 – 20 mg cellulase / g cellulose

Samples of suspension:

- Collected at various time points
- Boiled / refrigerated to deactivate enzyme

Determination of Yield Stress

A yield stress is the applied stress at which yield-stress fluids begin to flow. At imposed stresses below their yield stress, such materials act much like a solid. For example, while water and honey, both Newtonian fluids, form a smooth surface over time, mayonnaise, a yield-stress fluid, remains deformed after mixing with a spatula.

Yield Stress = 100 Pa

Honey

Mayonnaise

Yield Stress = 10 Pa

Transient Flow experiments

- Rheometer vane rotates steadily
- Earlier saccharification times:
  - Yield stress responded to concentration
- Later saccharification times:
  - Yield stress not observed

Oscillatory experiments

- Stress oscillated sinusoidally
- Yield Stress defined by:
  - Maximum of the elastic stress (G’ × peak strain)

Enzo-rheology: Rheology of Saccharified Corn Stover

- The yield stress of PCS suspensions decreases with biomass conversion.
- A rheological model developed by Wildemuth and Williams accurately correlates yield stress with particle volume fraction for both saccharified and un-saccharified PCS:

\[ \tau (\phi) = \left( \frac{1}{1 - \phi_{c}} \right)^{\lambda} \]

- Parameters with 95% CI:
  - \( \lambda = 1.4 \pm 0.6 \) Pa
  - \( \phi_{c} = 0.18 \pm 0.02 \) Pa
  - \( \phi_{c} = 0.41 \pm 0.01 \) Pa

Current and Future Research: Viscosity Modification

Numerous studies have been conducted to assess how surfactants and other chemical additives can be used to modify the binding properties of cellulase enzymes, resulting in enhanced saccharification kinetics and biomass conversions. Additionally, “drag reducing” polymers have long been known to lower the viscosity of water and petroleum, reducing pumping power and transport costs in pipelines.

In this work, we explore chemical additives to both enhance enzymatic saccharification and effect a reduction in the suspensions’ yield stress, a desirable synergy.

Summary

- A semi-empirical rheological model was used to relate volume fraction with yield stress:
  - A single set of model parameters is capable of characterizing yield stresses of suspensions in a number of enzymatic hydrolysis experiments across a range of enzyme concentrations.
  - It provides a good prediction of yield stress determined from particle volume fraction.

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